Supporting Information

Plasmon-Free SERS Self-monitoring of Catalysis Reaction on Au Nanoclusters/TiO_2 Photonic Microarray

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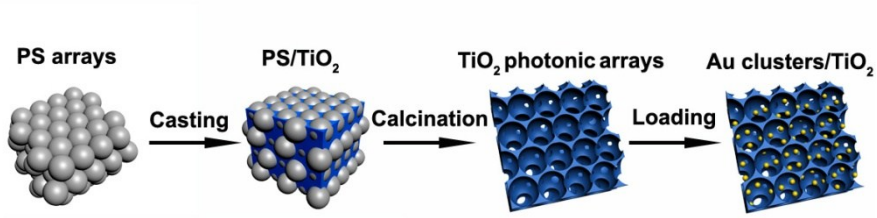

Scheme 1. Synthesis process of Au NCs/TiO_2 photonic array.

Experimental Section

Preparation of PS photonic crystal arrays: Polystyrene spheres (PS) were prepared according to a previous reference.[1] Before deposition of PS arrays, a hydrophilic treatment to silicon wafers was necessary. Silicon wafers were immersed into the solution of ammonium hydroxide and hydrogen peroxide (volume ratio is 1:2), and the mixture was boiled for 30 min. PS photonic crystal arrays were prepared via vertical deposition method as depicted in our previous work.[2] 400 μL of PS suspension was ultrasonically diluted by 25 mL H_2O in a 25 ml beaker. The hydrophilic silicon wafer was placed vertically in the beaker, and then kept static in 75 ^oC oven for 24 h.

Preparation of TiO_2 photonic arrays: The precursor solution of titania contained 5.6 mL Titanium isopropoxide (TTIP), 1 mL acetylacetone, 45 mL ethanol, 0.85 mL hydrochloric acid and 4.6 mL H_2O. A drop of the solution was spin-coated on PS microarray film. After hydrolysis at 75 ^oC for 48 h, the coated films were calcined at 450 ^oC for 2 h. The pore size of TiO_2 inverse opal is about 20% shrinkage compared with the sized of PS.

Preparation of Au NCs: Au NCs were synthesized according to a reported method.[3] 0.25 g $HAuCl_4$ and 0.28 g L-glutathione was dissolved in 300 mL ultrapure water. After stirring 1 h, the solution was heated to 70 ^oC and kept for 24 h. The obtained Au NCs solution shows light yellow color.

Preparation of Au NPs: Au NPs were prepared using a reported method with modification.[4] 0.01% $HAuCl_4$ solution 100 mL and L-glutathione 0.007 g were mixed and then heated to boiling, after that 2 mL 1% trisodium citrate solution was added immediately. After boiled for 10 min, the solution was cooled to form a Au NPs colloidal.

Loading of Au NCs on TiO_2 photonic arrays: The prepared TiO_2 inverse opal substrates were immersed into Au NCs solution for 48 h. After that the substrates were washed by water and dried.

Loading of Au NCs on Au NPs: The prepared Au NCs and Au NPs were mixed in the volume ratio of 1:3. Au NCs/Au NPs was obtained by centrifugation after stirring for 24 h.

Characterizations: X-ray powder diffraction (XRD) is analyzed on Rigaku D/max 2250 VB/PC apparatus. Scanning electron microscopy (SEM) images are obtained on TESCAN nova 3. Transmission electron microscopy (TEM) images are recorded on JEOL JEM-2100. UV-Vis spectra are measured on UV-Vis spectrophotometer (Shimadzu UV-2450), Fluorescence spectrum is collected on Edinburgh FLS980.

Raman spectroscopic study: Raman spectra were recorded (Reinshaw invia) using 785 nm laser (1% power, max power 500 mW) with 50× objective. Data acquisition time was kept for 10 s. For the monitoring of 4-NTP reduction by $NaBH_4$ on Au NCs/TiO_2 photonic array substrate, 100 μL of 10^{-3} M 4-NTP ethanol solution was first dropped on the substrates and dried in air. After that the substrates were washed repeatedly by water and dried. The substrates were immersed into 5 mL 0.01 M $NaBH_4$ solution. After a given time, the substrates were taken out and their Raman spectra were collected. For the monitoring on Au NCs/Au NPs, 100 μL the prepared Au NCs/Au NPs colloidal mixed with 100 μL 4-NTP ethanol solution, and the mixture was droped and dried on silicon wafer. After that the substrate was washed by water and dried. The substrates were immersed into 5 mL 0.01 M $NaBH_4$ solution. After a given time, the substrates were taken out and their Raman spectra were collected.

(1) Wang, J.; Wen, Y.; Ge, H.; Sun, Z.; Zheng, Y.; Song, Y.; Jiang, L. *Macromol. Chem. Phys.* **2006**, *207*, 596.
(2) Qi, D.; Lu, L.; Wang, L.; Zhang, J. *J. Am. Chem. Soc.* **2014**, *136*, 9886.
(3) Luo, Z.; Yuan, X.; Yu, Y.; Zhang, Q.; Leong, D. T.; Lee, J. Y.; Xie, J. *J. Am. Chem. Soc.* **2012**, *134*, 16662.
(4) Frens, G. *Nature* **1973**, *241*, 20.

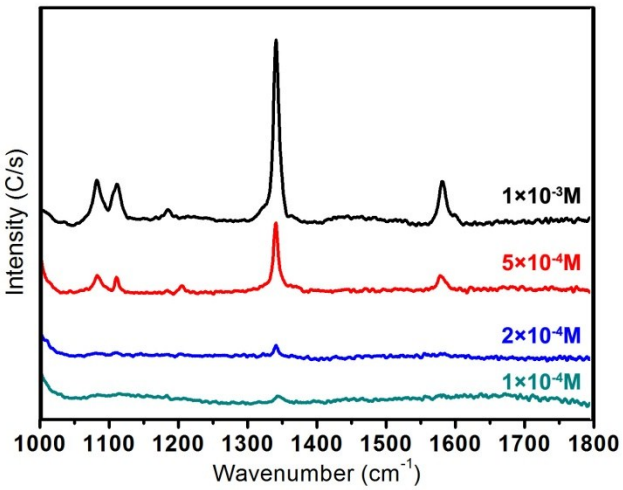

Figure S1. Raman spectra of 4-NTP with different concentrations adsorbed on TiO_2 photonic array.

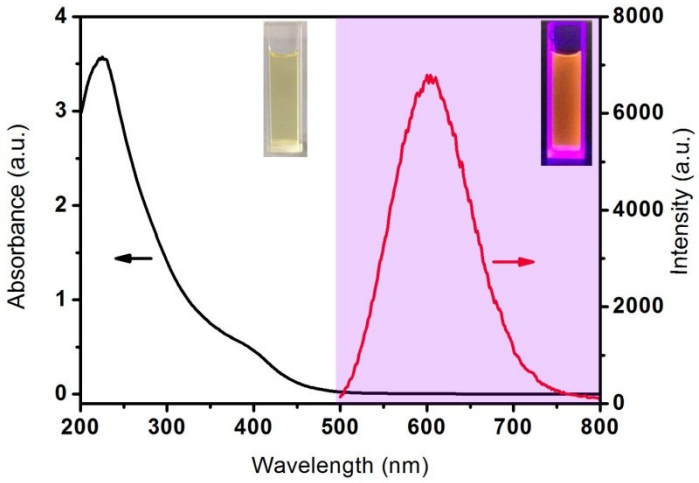

Figure S2. UV-Vis adsorption (black) and fluorescence spectrum (red) of Au NCs solution. The excitation wavelength is 365 nm. Insets are Au NCs solution under white light (left) and UV light (right) irradiation.

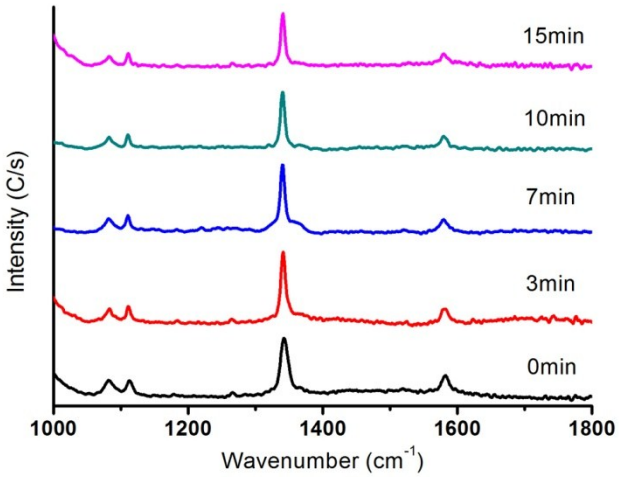

Figure S3. Raman spectra for monitoring the reduction of 4-NTP on TiO_2 photonic array without Au NCs.

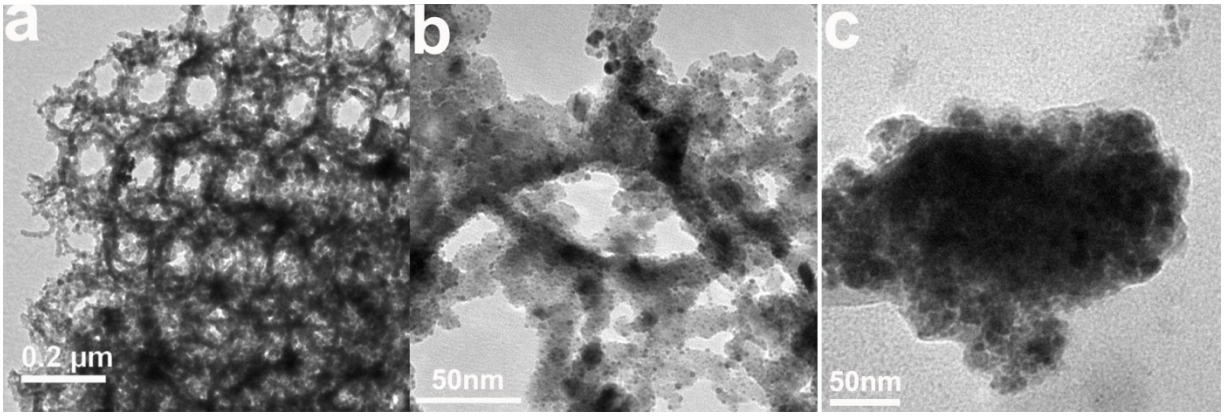

Figure S4. TEM images of Au NCs/TiO_2 photonic array (a and b) and Au NCs (c) after catalysis reaction. The comparison results indicate that aggregation of Au NCs is suppressed by loading on TiO_2 photonic array.

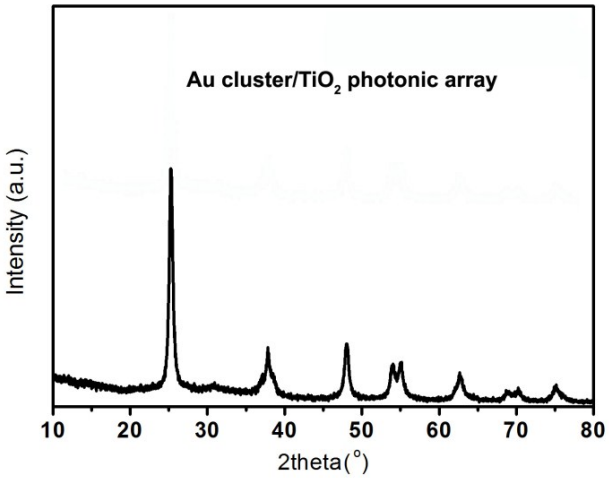

Figure S5. XRD pattern of Au NCs/TiO_2 photonic microarray. The patterns are attributed to anatase, and Au signals are not observed because of its tiny crystallite size.

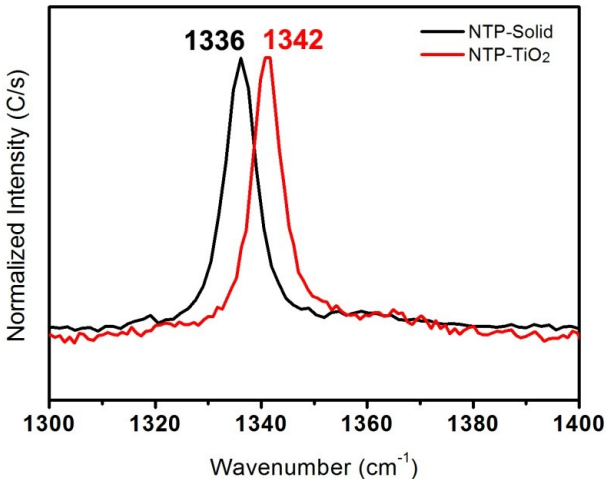

Figure. S6 Raman spectra of 4-NTP solid and 4-NTP adsorbed on TiO_2

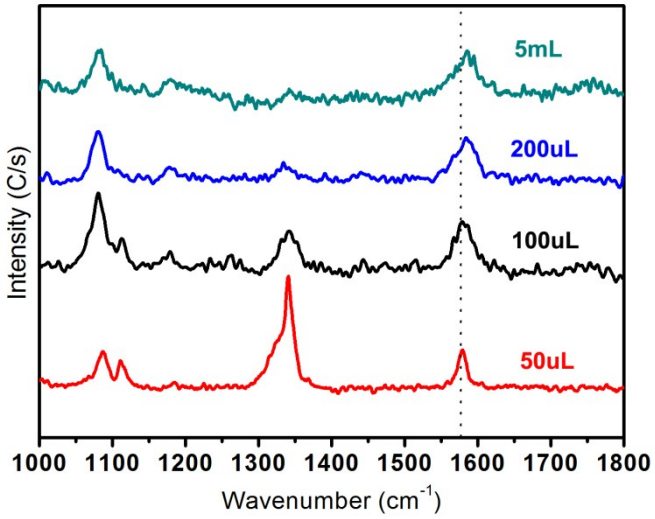

Figure S7. Raman spectra of 4-NTP reduced by different amount of $NaBH_4$ solution after 7 min on Au NCs/TiO_2 photonic array.

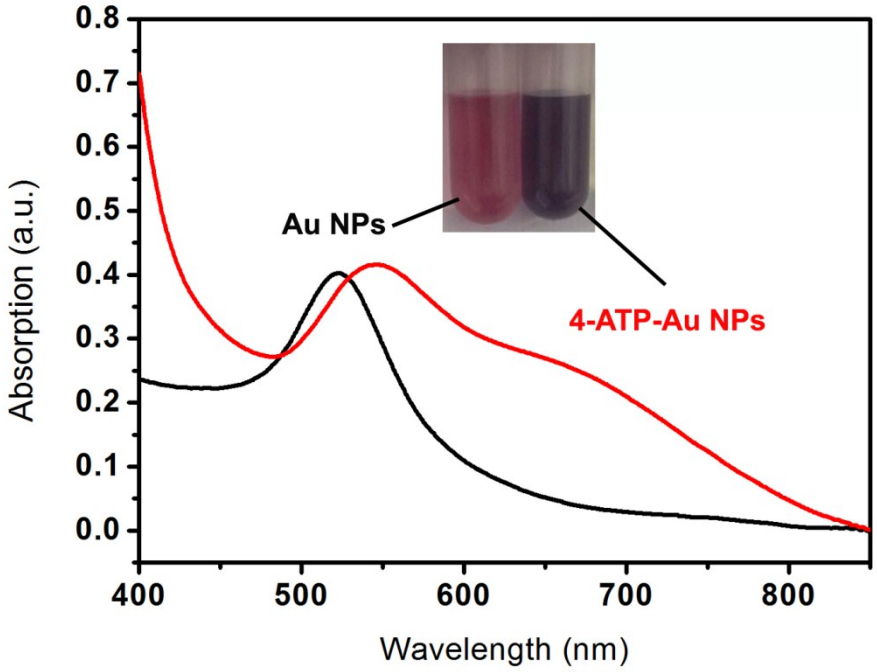

Figure S8. Absorption spectra of colloidal Au NPs (20 nm) mixed with ethanol (black curve) and 4-ATP ethanol solution (red curve).